

NOTE:

SUBJECT: Additional information and clarification for disulfoton RED

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Since the completion of the water assessment in the Environmental Exposure and Risk Assessment Document prepared by EFED (D237134, 08/26/00), as part of the Reregistration Eligibility Document (RED) for Disulfoton, additional information and/or surface water monitoring data and ancillary data (i.e., disulfoton usage in CA) has been considered as requested by SRRD. Also considered is a Lysimeter Study (MRID 449849-01) submitted by the registrant, as a 6(a)2 Action, which identified the potential leaching of radio-labeled (¹⁴C) disulfoton and metabolites. Several additional metabolites or degradates not previously identified in soil were detected in the leachate. Some of these including the oxygen analogs of the disulfoton sulfone and sulfoxide degradates were considered in HED's toxicology assessment.

This memo presents a discussion of the additional information and also provides clarification to several issues noted by SRRD.

I. Surface Water Monitoring (California)

The California Environmental Protection Agency's Department of Pesticide Regulation (CDPR) set up a surface water data base for storing surface water monitoring data collected in the state (<http://www.cdpr.ca.gov/docs/surfwatr/surfddata.htm>). This data base contains the results of studies conducted by a number of agencies and researchers and therefore, may have been included or reported elsewhere (e.g., STORET, NAWQA, CDPR). Because information reported in this data base may have been reported elsewhere, it is sometimes difficult to reconcile numbers of samples, number of wells, and numbers of detections. Data were entered into the data base by CDPR via raw data sheets, hard-copy data reports, electronic files, or downloaded from the Internet. Some specific information for each studied is included in the data base. The studies were generally not specifically targeted for disulfoton, although, it may have been included in the suite of analytes measured. Further, ancillary data may not be available to put the data into context such as specific use pesticide information, weather data, on site hydrology. Without the ancillary data it is difficult to interpret the monitoring results.

The CDPR data base contains the analytical results of 860 surface water samples collected, during 1991 to 1999, from ten counties which were analyzed for disulfoton (but not disulfoton degradates). The reported limits of detections ranged between 0.01 to 1.0 µg/L. The counties (number of samples) were Colusa (3), Contra Costa (1), Imperial (48), Merced (113), Sacramento (258), San Joaquin (93), Solano (4), Stanislaus (313), Sutter (6), and Yolo (21). Two disulfoton detections were reported in Stanislaus County, both at 0.06 µg/L (Foe, 1995, Krazter, 1998, and Dubrovsky et al., 1998). The first detection occurred in a sample collected on May 11, 1992 from the San Joaquin River at Laird Park near (site id 5015) Grayson California (Foe, 1995, CSWDB, 2000). The second detection, which was attributed to urban runoff by USGS, occurred in a sample collected on February 13, 1995 from the Farabuindo Storm drain (site id 5009) near Modesto California (Krazter, 1998, Dubrovsky, 1998, CSWDB, 2000).

The CDPR also keeps records of all agricultural pesticide used in California (CDPR Pesticide Use Report, 11/3/2000). Disulfoton usage by crop and year (1991 through 1998) for Stanislaus County, California is summarized in Table 1. The USDA Usual Planting and Harvesting Dates for Fresh Market and Processing Vegetables. (USDA Handbook # 507) indicates that in California disulfoton is (can be) applied throughout the year (Table 2). The highest use in Stanislaus County, during this period, occurred in 1992 when about 1290 lbs of disulfoton was applied, in August, to cauliflower. Since the disulfoton (in 1992) was applied after the disulfoton was detected in the San Joaquin River, the 1992 use on cauliflower does not appear to be the disulfoton source. The 1991 use of disulfoton was third highest, thus the source could be related to earlier applications of disulfoton, unreported use, urban use, or use in a county other than Stanislaus. In adjacent San Joaquin County 23,914 lbs of disulfoton (13,544 lb aerial, 10,370 lb ground) (13029 - aerial, 10,828 - ground acres treated) was applied to asparagus in 1992. Another adjacent county, Merced, reported the use of 251.1 lbs on (121.5 lbs aerial, 129.6 ground) cauliflower, 15 lbs (ground) on cotton, and 206.6 lb (ground) on peppers. It is possible that the 1992 detection was result of the use of disulfoton in adjacent counties. The 1995 detection was attributed to urban runoff, thus urban usage. Urban disulfoton usage information is not known.

Table 1. Agricultural disulfoton use in Stanislaus County, CA for 1991 through 1998 ¹
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Crop	Year	Application method	lbs applied	acres treated (# of fields)	Avg. rate
Cauliflower	1991	Ground	279	230 (3)	1.21
Asparagus ^{2,3}	1992	Ground	8.1	7(1)	1.16
Cauliflower ³	1992	Ground	1162.2	1074(18)	1.08
		Aerial	129.6	125(2)	1.03
Broccoli	1993	Ground	8.1	7(1)	1.16
Cabbage	1993	Ground	60.7	60(1)	1.01
Cauliflower	1993	Ground	501.0	458(8)	1.11
Asparagus	1994	Ground	18.2	18(1)	1.01
		Aerial	18.2	18(1)	1.01
Broccoli ⁴	1995	Ground	66.7	55(2)	1.21
Cauliflower	1996	Ground	72.7	60(1)	1.21
Barley	1997	Aerial	121.5	120(1)	1.01
Beans, Dried	1997	Ground	35.4	35(1)	1.01
Beans, Dried	1997	Ground	20.25	20(1)	1.01
Cauliflower	1997	Ground	91.0	75(1)	1.21
Wheat, General	1997	Aerial	81.2	107(1)	0.76
Asparagus ²	1998	Aerial	33.5	33(1)	1.01
Barley	1998	Aerial	81.0	80(1)	1.01
Cauliflower	1998	Ground	72.7	60(1)	1.21

¹ California's Department of Pesticide Regulation, Pesticide Use Reports, 11/03/00

² Asparagus, spears, ferns, etc.

³ Disulfoton applied in August 1992.

⁴ Disulfoton applied in September 1995

Table 2. Usual planting dates for vegetables in California¹

Crop and season	Usual Planting Dates
Asparagus	January 1 to March 31
Broccoli - winter	September 1 to November 30
Broccoli - spring	December 31 to March 31
Broccoli - summer	April 1 to June 30
Broccoli - fall	July 1 to August 31
Cabbage - winter	September 1 to October 31
Cabbage - spring	November 1 to February 28
Cabbage - summer	March 1 to May 31
Cabbage - fall	June 1 to August 31
Cauliflower- winter	September 1 to November 30
Cauliflower- spring	December 1 to April 1
Cauliflower- summer	March 1 to May 31
Cauliflower- fall	June 1 to August 31
Cucumbers - spring (fresh market)	January 1 to March 31
Cucumbers - summer (fresh market)	April 1 to June 30
Cucumbers - fall (fresh market)	July 1 to August 30
Cumcumbers (processing)	April 10 to June 10

¹ USDA, 1997. Usual Planting and Harvesting Dates for Fresh Market and Processing Vegetables. Crop Reporting Board Statistical Reporting Service. USDA Handbook # 507. Government Printing Office, Washington, DC.

Citations:

Baker, F.C., K. Aldcroft, and M.F. Lenz. 1999. Determination of Potential Leaching of ¹⁴C-Disulfoton and metabolites using field lysimeters in two climatic regions of California. Bayer Report No. 108825. (MRID 449849-01).

Foe, C. 1995. Insecticide concentrations and invertebrate bioassay mortality in agricultural return water from the San Joaquin basin. Central Valley Regional Water Quality Control Board,

Sacramento, CA.

Howard, P.H. (1991). Disulfoton p. 309 - 318. In. Volume III. Pesticides. Handbook of Environmental Fate and Exposure Data. For Organic Chemicals. Lewis Publishers, Inc. Chelsea, Michigan.

Kratzer, C. R. 1998. Pesticides in storm runoff from agricultural and urban areas in the Toulumne River Basin in the vicinity of Modesto, California. USGS National Water Quality Assessment Program. Water Resources Investigations Report.

Dubrovsky, N.M., C.R. Kratzer, L.R. Brown, J.M. Gronberg, and K.R. Burow. Water Quality in the San Joaquin-Tulare Basins, California, 1992-95. USGS Circular 1159. USGS Denver, CO.

USDA, 1997. Usual Planting and Harvesting Dates for Fresh Market and Processing Vegetables. Crop Reporting Board Statistical Reporting Service. USDA Handbook # 507. Government Printing Office, Washington, DC.

II. Degradates in Lysimeter Leaching Study

Study Title: Determination of Potential Leaching of ^{14}C -Disulfoton and metabolites using field lysimeters in two climatic regions of California. (MRID 449849-01).

A soil dissipation study (unreviewed), where disulfoton (Di-Syston 8, EPA Reg. No. 3125-307) was applied in five applications to in-field lysimeters, was conducted at Watsonville and Ripon, California. The first application (4.0 lb ai/ac) of disulfoton was "directly to soil". The wheat (*Anza*) was planted then followed by a second side dressing application (3.0 lb ai/ac), and three foliar applications at 1 lb ai/ac each, for a total of 10 lb ai/ac. Disulfoton was applied at Watsonville on April 28, June 14, June 22, June 30, and July 10, 1995. At the Ripon site, disulfoton was applied on June 7, July 6, July 18, July 16, and August 7, 1995. The Watsonville study was conducted for 18 months and the Ripon study was conducted for 24 months. Three mature wheat harvests plus one immature wheat harvest were obtained from the planted lysimeters. The application scenario used in this study does (i.e., 5 applications @ 4, 3, 1, 1, and 1 lb ai/ac) not correspond with the registrants proposed label changes (2 applications @ 0.75 lb ai/ac). One of three tracers, potassium bromide, sodium chloride, and sodium fluoresceinate, was also applied to the lysimeters. The bromide tracer and the disulfoton degradates leached during the same time period, suggesting similar transport mechanisms and perhaps mobility.

The range of parent disulfoton and degradates, expressed as radioactivity, for soil (both sites) and the maximum leachate (each site) are listed in Table 3. Soil recovery at the different sampling times (1 month after application to end of study) ranged from 100% to 15.8% at Watsonville and 68.2% to 9.5% at the Ripon site. The percent recovery of applied radioactivity in the leachate at the different sampling dates ranged from 0.7% to 10.2% (at 12 to 18 months after application) at the Watsonville site and 0.1% at the Ripon site (at 24 months after

application). More leaching occurred at Watsonville because there was more rainfall. The highest concentrations of degradates were disulfoton sulfonic acid, disulfoton oxygen analog sulfonic acid with lesser concentrations of DEP, DEPT, ethanol, and bicarbonate. Several disulfoton residues identified in the toxicological expression include parent disulfoton, disulfoton sulfone and disulfoton sulfoxide, and the oxygen analog form of the sulfone and sulfoxide were also found in leachate, but a lower concentrations. This lysimeter studies demonstrate that the sulfone and sulfoxide (and oxygen analog) degradates are more mobile and persistent than parent disulfoton, thus having a greater probability to contaminate ground water. Uncertainties associated with this study includes the number and rate of the disulfoton applications do not correspond with current or proposed labels and many issues exist and remain unresolved as to extrapolating results from lysimeter studies to field scale processes.

Based on the results of this study, the concentrations of oxygen analogs of the D. sulfoxide and D. sulfone in the leachate are about the same order of magnitude as the disulfoton sulfoxide and disulfoton sulfone. This would suggest that the estimates of the exposure by only considering the sulfoxide and sulfone forms would be under estimated. For this study maybe by a factor of 2. But it is difficult to determine this because of the multiple applications of disulfoton. The disulfoton must be transformed to disulfoton sulfoxide and sulfone before the oxygen analogs are formed. Thus the different residues will be forming and declining at different rates.

Table 3. Disulfoton toxic residues in lysimeter leachate and toxic and non-toxic residues in soil.				
Chemical	Media	ID	Max. radioactivity (ppm)	
			Ripon	Watsonville
Disulfoton	Leachate	PSS	0.0003	0.0002
Disulfoton oxygen analog	Leachate	Demeton-S		
Disulfoton sulfoxide	Leachate	PSSO	0.0003	0.0079
Disulfoton oxygen analog sulfoxide	Leachate	POSO	0.0010	0.0034
Disulfoton sulfone	Leachate	PSSO ₂	0.0005	0.0013
Disulfoton oxygen analog sulfone	Leachate	POSO ₂	0.0030	0.0020
Disulfoton sulfonic acid ¹	Leachate	SSO ₃	0.1146	0.6205
D. oxygen analog sulfonic acid ¹	Leachate	OSO ₃	0.0145	0.3255
Ethanol ¹	Leachate	EtOH	0.0097	0.0350
Bicarbonate ¹	Leachate	HCO ₃	0.0053	0.0481

Diethylphosphate ¹	Leachate	DEP	0.0062	0.0383
Diethylphosphorothioate ¹	Leachate	DEPT	0.0013	0.0342
			Range of soil extracts (ppm) from Watsonville or Ripon.	
Disulfoton	Soil	PSS	0 to 1.841 (time = 0)	
Disulfoton sulfoxide	Soil	PSSO	0 to 0.755	
Disulfoton oxygen analog sulfoxide	Soil	POSO	0 to 0.834	
Disulfoton sulfone	Soil	PSSO ₂	0 to 1.322	
Disulfoton oxygen analog sulfone	Soil	POSO ₂	0 to 0.102	
Disulfoton sulfonic acid ¹	Soil	SSO ₃	0 to 0.744	
D. oxygen analog sulfonic acid ¹	Soil	OSO ₃	0 to 0.027	

¹ Not included in toxic assessment.

III. Data Gaps:

A number (5) of disulfoton residues (metabolites or degradates) included in the toxicological expression; parent disulfoton, disulfoton sulfone and disulfoton sulfoxide, and the oxygen analog form of the sulfone and sulfoxide, were found in leachate and soil of a lysimeter study. This study demonstrated that the sulfone and sulfoxide and the oxygen analog forms of the sulfone and sulfoxide degradates are more mobile and persistent than parent disulfoton, thus having a greater probability to contaminate ground water. With the implementation of FQPA, OPP must be able to estimate pesticide residue concentrations in drinking water to determine possible risk associated with pesticide exposure from drinking water. Pesticide residue levels in water are either measured through monitoring or estimated through the use of computer models. Monitoring programs for both surface water and ground water have generally not included degradates, so modeling methods must be used to estimate exposure levels.

The models used to estimate ground water and surface water concentrations require pesticide specific fate information (dissipation rate and/or half-life and binding potential or sorption (K_d or K_{oc})) for the parent compound and degradates. The estimates of disulfoton residue concentrations in ground and surface water were modeled in the RED for both parent disulfoton and total disulfoton residue (TDR). TDR was the sum of the disulfoton, disulfoton sulfoxide, and disulfoton sulfone. The decline of the TDR followed a first order half-life decline. The mobilities of the degradates were assumed to be equal to the parent. The oxygen analog of disulfoton sulfoxide and disulfoton sulfone residues were not included in the exposure assessment, as these data (persistence and mobility) were not available. Because the exposure

estimate does not include the oxygen analog degradates the exposure may be underestimated. Data suggests that disulfoton and disulfoton sulfoxide, and disulfoton sulfone may degrade rapidly in water via photolysis. Whether this holds true for the oxygen analog forms is not known. Photolysis would not be a factor in ground water or in surface water with reduced or restricted light penetration. Hydrolysis at relevant environment temperatures is also very slow ($T_{1/2}$ 1174, 323, and 231 days at pH 4, 7, and 9, respectively and 20°C). The aerobic soil metabolism shows that the degradates are more persistent. Literature has also questioned whether disulfoton residues are susceptible in water to biodegradation. Therefore, the aerobic and anaerobic aquatic metabolism of disulfoton residues is needed to confirm disulfoton degradation in ground water and surface water, when photolysis does not occur. Data on the fate of parent disulfoton in water and these degradates in soil and water would allow additional characterization of the risks they present to non-target organisms and drinking water..

The following environmental fate requirements have not been satisfied for disulfoton sulfone, D. sulfone and the oxygen analog forms of the D. sulfone and D. sulfoxide

162-1: Aerobic soil metabolism

The following environmental fate requirements have not been satisfied for disulfoton, disulfoton sulfone, D. sulfone and the oxygen analog forms of the D. sulfone and D. sulfoxide

162-2: Anaerobic soil metabolism

The following environmental fate requirements have not been satisfied for disulfoton, D. sulfoxide, D. sulfone, and the oxygen analog forms of the D. sulfone and D. sulfoxide:

162-3: Anaerobic Aquatic Metabolism

162-4: Aerobic Aquatic Metabolism

163-1: Mobility - Leaching and adsorption/desorption for D. sulfone, D. sulfoxide, and the oxygen analog forms of the D. sulfone and D. sulfoxide.

In Bayer's, May 9, 2000 response to Disulfoton, Input to Phase V of the Risk Assessment Process, List A, Case 0102, OPP Docket Control No. 34165B from James Lee Kunstman, PhD Registrations Manager, Insecticides indicated that EFED should use aqueous photolysis, hydrolysis, and foliar half-life values that reflect total disulfoton residues when attempting to quantify total disulfoton residues in the water. EFED agrees. Bayer should submit aqueous photolysis (161-2), hydrolysis (161-1), and foliar half-life (or rate)(non-guideline) data for disulfoton sulfone, disulfoton sulfoxide and oxygen analog forms of the D. sulfone and D. sulfoxide degradates.

4. EFED Degradates of Concern

On February 6, 1992 the Environmental Fate and Ground Water Branch enacted a policy

regarding the level of degradates that are of concern for the purpose of providing OPP with an integrated environmental fate and transport assessment. The policy was developed for residues in the soil not water. This policy was enacted prior to the implementation of FQPA and the aggregate exposure issue was considered by the Agency.

The policy stated that "Studies conducted to satisfy EFGWB data requirements must identify and characterize those degradates present at levels greater than or equal to 0.01 ppm or 10% of applied, whichever is less, whether or not there is a known toxicological concern about those degradates. These guidelines however, do not preclude requiring additional information on a case-by-case basis for those degradates found at lower levels, but identified to have toxicological or ecological concerns."

V. 2. Dietary Risk from Drinking Water, page 10 - need to present data to support statement?

A lysimeter study (MRID 449849-01) submitted by the registrant, as a 6(a)2 Action, which identified the potential leaching of radio-labeled (^{14}C) disulfoton and metabolites including disulfoton sulfone and disulfoton sulfoxide as well as the oxygen analogs of the disulfoton sulfone and sulfoxide degradates. Howard (1991) reports that total disulfoton residue, including possibly the sulfone, sulfoxide, and oxygen analogs, have been observed in paddy soils for more than 12 weeks. Aerobic soil metabolism studies show that parent disulfoton is not very persistent, with non-first order half-lives of less than 6 days. The aerobic soil metabolism half-life is > 17 days for disulfoton sulfone and > 150 days for disulfoton sulfoxide. The calculated aerobic soil metabolism half-life for total disulfoton residues (disulfoton, disulfoton sulfone, disulfoton sulfoxide) is > 200 days. The data to assess the persistence of the degradates including the oxygen analogs forms of the degradates in soil and water has not been submitted by the registrant.

Howard (1991) reports that studies have been somewhat conflicting with regards to the differentiation between chemical and biological degradation of disulfoton in soil. Thus, it is unclear whether biodegradation occurs in natural water. The oxidation of disulfoton to disulfoton sulfoxide apparently occurs rapidly when sunlight is able to penetrate the water. Thus, in ground water or where sunlight is unable to penetrate due to depth or sediment, the persistence of disulfoton and degradates could be greatly increased if biodegradation is not important.